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DEVELOPMENT OF A TURN-KEY SYSTEM FOR HAZARDOUS WASTES ANALYSIS

P. Yang, M. Yang, J. Semmler, G. Crawford, Trace Organics Section, Laboratory Services Branch, Ontario Ministry of the Environment, Rexdale, Ontario, M9W 5L1

SUMMARY

A turn-key hazardous wastes analysis system has been developed using Fourier transform attenuated total reflectance infrared spectrometry, artificial intelligence assisted library searching and an automated infrared interpreter. Both the library searching and the infrared interpreter take advantage of the portability, the computing power and the mass data storage available for PC systems and is demonstrated to be a cost effective tool to assure consistent data interpretation. This turn-key system has a 10 nanogram detection limit and provides fast sample turn-around-time. The possibility of direct sample analysis without any clean-up process is demonstrated. Preliminary results from this developmental work indicate the possible improvement of sample throughput by as much as 300%.

INTRODUCTION

This automated infrared interpreter was developed on an IBM personal computer (PC) running under the Microsoft disk operating system (DOS). Based on the original Merck Sharp & Dhome Research Laboratory Program for the Analysis of Infrared Spectra (PAIRS) (1,2), this infrared interpreter, PC PAIRS⁺, is capable of analyzing infrared spectra measured with a wide variety of spectrophotometers.

Modifications have been made to PAIRS to enable the application of both artificial

intelligence and library searching. Furthermore, a new algorithm has been devised to combine the results from the library searching and the PAIRS program to obtain high confidence level interpretational data. Major functionalities of the PC PAIRS⁺ are illustrated in Figure 1.

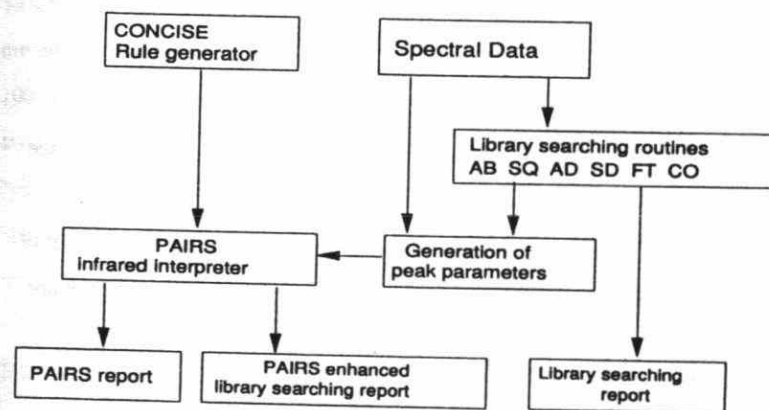


Figure 1. Functionalities of PC PAIRS⁺

All software was developed on a Magus Data Technology (Richmond Hill, Ontario) 80386/80387 IBM DOS PC running at a clock speed of 20 MHz. The

original PAIRS and the infrared interpretation rule generator, the Computer Oriented Notation Concerning Infrared Spectral Evaluation (CONCISE) (3,4) language, were obtained from the Quantum Chemistry Program Exchange (Bloomington, Indiana, Catalog # QCPE 426). The programs were downloaded into the PC via a RS-232 line from a VAX 780 system. Both programs were modified and converted to standard Ryan McFarland FORTRAN (Phoenic Computer Products, Norwood, MA) conventions, compiled and run on the same PC.

The library searching subprogram used five search algorithms. They are: absolute difference (AB), square of absolute difference (SQ), absolute difference of first derivative (AD), square of difference of first derivative (SD) and time domain cross correlation (FT). One additional algorithm was developed as part of this project to combine the library searching results from the first five algorithms, the combined algorithm (CO).

EXPERIMENTAL

A. Chemicals and Method of Analysis. A total of 67 oil and grease samples were measured in this work. These samples are standards of the most commonly encountered petroleum hydrocarbons and greases in the province of Ontario. A Barnes (SpectraTech Inc., Stamford, CT) micro circle cell accessory was used to measure the attenuated total reflectance (ATR) spectra of the samples. These spectra then formed the MOE Oil & Grease Library.

Several ATR infrared spectra were generated to test the software and the Oil & Grease library. Typically, about 2 ml of oil samples were used to spike one litre of tap water. Using the standard MOE method for the solvent extractable (5) the oils was extracted from the water sample using dichloromethane. Upon evaporation of the solvent the infrared spectrum of the residue was measured

B. Instrumentation. Either a BOMEM MB-100 (Quebec, Quebec) or a Nicolet 5SX (Madison, WI) Fourier transform infrared (FT-IR) spectrometer was used to measure the spectra. An optical retardation of 0.25 cm was used to signal average 100 single sided interferograms with a resolution of 2 cm^{-1} . The BOMEM FT-IR used an IBM DOS PC computer for the data collection and manipulation. For the Nicolet 5SX FT-IR, a Nicolet 620 data system was used to serve the purposes. Spectra measured with the BOMEM FT-IR were used without any change. For spectra measured on the Nicolet FT-IR a NICOMPC communication software (Nicolet Inc., Madison, WI) was used to download the spectra into the PC via a RS-232 line. The downloaded spectra were then used to create the spectral library.

RESULTS AND DISCUSSIONS

Figure 2 illustrates the process employed by PC PAIRS⁺ in the evaluation of unknown spectra and report generation. Library searching was used for the positive identification of unknowns. In order to minimize the effect of noise and baseline problems of the infrared spectrum, results from all five library searching

algorithms (AB, SQ, AD, SD, CO) were combined to determine the best match for the unknown. Table 1 illustrates a typical library searching report from this turn-key system. The test sample used was IOSOL 1520, a common paint thinner used for the oil based paint. The library searching routine was set to list the five best matches from each individual routine. From Table 1, the AB and the SQ algorithms fail to identify the unknown from the Oil & Grease library. The CO method, on the other hand, successfully identified this unknown and many others, supporting its use as the method of choice for the library searching.

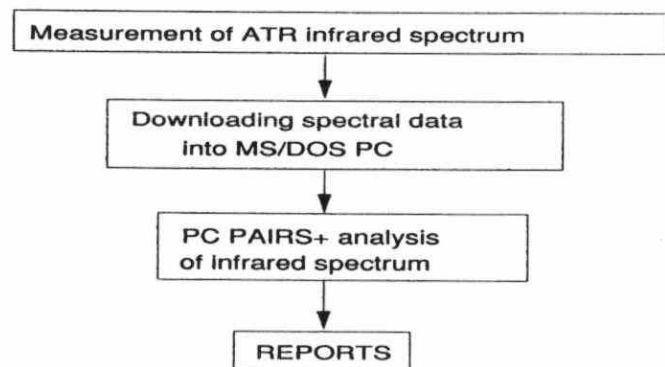


Figure 2. Procedures for a typical unknown sample analysis using the turn-key system.

Although the oil library with the five search algorithms have been successful for the identification of many routine sample analysis, we have encountered some situations where PAIRS⁺ proved to be superior. To illustrate this we added digital noise to a spectrum of Turbo A-1 oil to simulate the spectrum of an unknown organic extracted with dichloromethane. This spectrum was then searched through our oil library using CO algorithm. The result is shown in Figure 3. From this Figure, it is clear that all three matches and the test spectrum have identical spectra which makes the identification of the test spectrum from the library searching results impossible. Using PAIRS⁺, although interpretational results from the infrared interpreter indicated the presence of methyl and methylene group in the unknown and in all three matches, the probability order for the "functional groups" identifies the match #1 as the correct identification. These results are listed in Table 2. By comparing the probabilities obtained for match #1 with those obtained for matches #2 and #3 one can conclude that only match #1 is the correct answer.

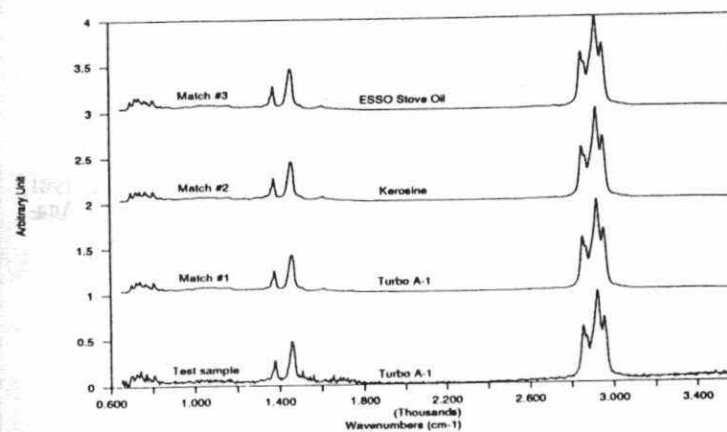


Figure 3. Library searching results for the test sample using the CO method. The close resemblance between the unknown and the three matching spectra complicates the task of positive identification requiring.

A turn-key system has been developed to utilize artificial intelligence and the positive identification capability of the library searching. The CO algorithm which combines results from five different library searching routines can obtain high quality library searching data. The typical analysis time of this turn-key system, including the data entry, the library searching and the final PAIRS⁺ interpretation, is about five minutes per sample. PC PAIRS⁺ not only increases the sample throughput of routine sample identification in the laboratory but also standardizes the procedure of infrared data interpretation. Current system is with an enhanced user interface and takes advantage of the ready access and user friendly nature of PC computer systems, therefore, can be an invaluable training system in the laboratory.

1. Woodruff, H.B. and Munk, M.E., Analytica Chimica Acta, **95**, 13 (1977).
2. Woodruff, H.B. and Smith, G.M., Anal. Chem., **52**, 2321 (1980).
3. Woodruff, H.B. and Smith, G.M., Analytica Chimica Acta, **133**, 545 (1981).
4. Tomellini, S.A., Hartwick, R.A., Stevens, J.M. and Woodruff, H.B., Analytica Chimica Acta, **162**, 227 (1984).
5. Ontario Ministry of the Environment Method SXT-E3201A.1, Rexdale, Ontario, Canada.

The sample spectrum is: IOSOL 1520
The reference library is: >>>> The Oil Library <<<<<

(The FT Method)

- * Match #1 with probability of >>>>>> 0.020430 <<<<<<<
File # 35: IOSOL 1520, TRACE ORGANICS
* Match #2 with probability of >>>>>> 0.024283 <<<<<<<
File # 19: ESSO REGULAR GASOLINE, TRACE ORGANICS
* Match #3 with probability of >>>>>> 0.026579 <<<<<<<
File # 21: ISOPAR 'M', TRACE ORGANICS
* Match #4 with probability of >>>>>> 0.029905 <<<<<<<
File # 32: ISOPAR 'K', TRACE ORGANICS
* Match #5 with probability of >>>>>> 0.052817 <<<<<<<
File # 4: DISTILLED ISOPAR H, TRACE ORGANICS

(The AB Method)

- * Match #1 with probability of >>>>>> 27.904972 <<<<<<<<
File # 16: IOSOL I125, TRACE ORGANICS
* Match #2 with probability of >>>>>> 30.336798 <<<<<<<<
File # 32: ISOPAR® K, TRACE ORGANICS
* Match #3 with probability of >>>>>> 30.400099 <<<<<<<<
File # 21: ISOPAR® M, TRACE ORGANICS
* Match #4 with probability of >>>>>> 32.325081 <<<<<<<<
File # 53: TURBO FUEL, TRACE ORGANICS
* Match #5 with probability of >>>>>> 32.441692 <<<<<<<<
File # 27: IOSOL 2024, TRACE ORGANICS

(The AD Method)

- * Match #1 with probability of >>>>>> 2.182141 <<<<<<<
File # 35: IOSOL 1520, TRACE ORGANICS
* Match #2 with probability of >>>>>> 3.216939 <<<<<<<
File # 32: ISOPAR 'K', TRACE ORGANICS
* Match #3 with probability of >>>>>> 3.284418 <<<<<<<
File # 21: ISOPAR 'M', TRACE ORGANICS
* Match #4 with probability of >>>>>> 4.126999 <<<<<<<
File # 16: IOSOL 1125, TRACE ORGANICS
* Match #5 with probability of >>>>>> 4.243579 <<<<<<<
File # 24: VARSOI 3135, TRACE ORGANICS

(The SD Method)

7) AROMATIC	0.00
8) AROM-MONOSUBST	0.00
9) Z1	0.00
10) AROM-1.2-SUBST	0.00

Interpretation for library match # 2.....

Spectral data summary for: Kerosine, TRACE ORGANICS

The solvent is: neat

No empirical formula given

There are 24 peaks			
Line	Width	Intensity	Location
1	sharp	1	729
2	sharp	1	739
3	sharp	1	771
4	sharp	1	918
5	sharp	1	964
6	sharp	1	980
7	sharp	1	1007
8	sharp	1	1043
9	sharp	1	1055
10	sharp	1	1063
11	sharp	1	1066
12	sharp	1	1074
13	sharp	1	1090
14	sharp	1	1097
15	sharp	1	1124
16	sharp	1	1151
17	sharp	1	1169
18	sharp	1	1340
19	sharp	3	1365
20	average	4	1379
21	average	5	1464
22	average	6	2873
23	broad	7	2927
24	average	10	2956

Printout is sorted by probability:

Group name	Probability
1) METHYL	0.88
2) ACID	0.75
3) METHYL-GEMDI	0.55
4) KETAL	0.45
5) AMINE	0.40
6) AMINE-TERTIARY	0.40
7) ACETAL	0.40
8) NH3+	0.25
9) MERCAPTAN	0.25
10) METHYLENE	0.22
11) AROMATIC	0.05
12) HETEROAROMATIC	0.01
13) PYRIDYL	0.01
14) PYRAZYL	0.01

15) PYRIMIDYL	0.01
16) PURINE	0.01
17) INDOLE	0.01
18) PYRROLE	0.00
19) FURAN	0.00
20) THIOPHENE	0.00

Interpretation for library match # 3.....

Spectral data summary for: ESSO Stove Oil, TRACE ORGANICS

The solvent is: neat

No empirical formula given

There are 22 peaks

Line	Width	Intensity	Location
1	average	1	739
2	sharp	1	773
3	sharp	1	918
4	sharp	1	964
5	sharp	1	1007
6	sharp	1	1032
7	sharp	1	1038
8	sharp	1	1045
9	sharp	1	1055
10	sharp	1	1059
11	sharp	1	1068
12	sharp	1	1082
13	sharp	1	1103
14	sharp	1	1122
15	sharp	1	1151
16	sharp	1	1169
17	sharp	3	1365
18	average	4	1379
19	average	5	1460
20	average	6	2871
21	sharp	7	2927
22	average	10	2956

Printout is sorted by probability:

Group name	Probability
1) METHYL	0.93
2) ACETAL	0.84
3) METHYL-GEMDI	0.55
4) KETAL	0.52
5) METHYLENE	0.49
6) AMINE	0.40
7) AMINE-TERTIARY	0.40
8) AROMATIC	0.05
9) ACID	0.05
10) HETEROAROMATIC	0.01
11) PYRIDYL	0.01
12) PYRAZYL	0.01
13) PYRIMIDYL	0.01
14) PURINE	0.01
15) INDOLE	0.01



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